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Über die Synthese von Methionol.

Von Shiro AKABORI und Takeo KANEKO.

(Eingegangen am 14. Dezember 1938.)

Vor zwei Jahren haben die Verfasser[1] von dem Vorkommen des γ-Methylmercapto-propylalkohols im „Shoyu" (der japanischen Suppenwürze) als Hauptprinzip des Aromas berichtet und für den schwefelhaltigen Alkohol den Namen „Methionol" vorgeschlagen, weil es kaum zu bezweifeln ist, dass der Alkohol im „Shoyu" aus Methionin folgenderweise entsteht.

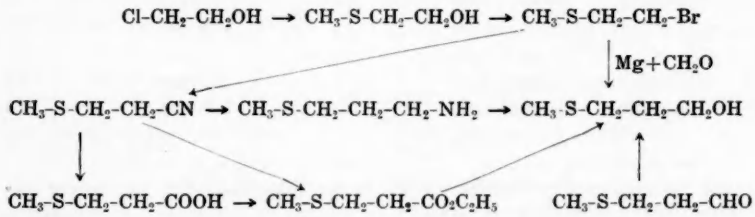
$$CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{-}COOH \rightarrow CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CHO \rightarrow CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$

Methionin — Methionol

Die Synthese des Methionols ist von uns nach W. R. Kirner[2] durch Umsetzung von Trimethylenchlorhydrin mit Natrium-methylmercaptid durchgeführt worden.

$$CH_3SNa + Cl\text{-}CH_2\text{-}CH_2\text{-}CH_2OH \rightarrow CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$

Es sind aber noch verschiedene andere, vom Äthylenchlorhydrin ausgehende Wege zur Synthese von Methionol möglich, z.B. wie folgt.



Wir haben alle die oben angegebenen Wege geprüft, konnten aber in keinem Fall befriedigende Ausbeuten erhalten. Nun ist es uns auffallenderweise geglückt, eine neue sehr einfache Synthese aufzufinden. Diese beruht darauf, dass sich Methylmercaptan an die Doppelbindung des Allylalkohols nach folgender Gleichung anlagert.

$$CH_2{=}CH\text{-}CH_2OH + CH_3SH = CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$

Ohne Katalysator geht die Reaktion äusserst langsam vor sich, lässt sich aber durch Zusatz von geeigneten Katalysatoren (z.B. Quecksilber-

(1) *Proc. Imp. Acad.* (Tokyo), **12** (1936), 131.
(2) *J. Am. Chem. Soc.*, **50** (1928), 2446.

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salz) erheblich beschleunigen. Interessanterweise ist Sauerstoff als Katalysator stark wirksam ebenso wie bei der Anlagerung von Bromwasserstoff an die Doppelbindung des Allylbromids.[3] Der Einfluss des Lichtes auf die Reaktion ist auch merklich, wie aus der folgender Tabelle ersichtlich ist. Die Tabelle zeigt die Resultate unserer Experimente, die folgenderweise ausgeführt worden sind.

Eine Mischung von 10 g. Allylalkohol und 10 g. Methylmercaptan wurde unter Zusatz (oder ohne) Katalysator in einer geschlossener Röhre, jeweils verschiedene Zeitenlang bei wechselnden Temperaturen gehalten. Die Reaktionsflüssigkeit wurde unter vermindertem Druck der fraktionierenden Destillation unterworfen. Die bei 99–101°/23 mm. übergehende Fraktion erwies sich als Methionol. Es wurde in Form seines Doppelsalzes mit Quecksilberchlorid ($C_4H_{10}OS \cdot 2\frac{1}{2}HgCl_2$, Schmp. 128–128.5°) identifiziert.

Nr. der Experimente	Katalysator		Atmosphäre über der Reaktionsflüssigkeit	Reaktionstemperatur	Reaktionsdauer	Ausbeute an Methionol in g.	Ausbeute in %
1	$(CH_3S)_2Hg$	0.5 g.	Luft	110°	24 Stunden	7.5	41
2	—	—	„	„	„	1.5	8
3	$(CH_3S)_2Hg$	0.5 g.	„	140–150°	5 Stunden	11	61
4	$(CH_3COO)_2Hg$	0.6 g.	„	140–160°	22 Stunden	11	61
5	$(CH_3S)_2Hg$	0.5 g.	O_2	Zimmertemp.	1 Monat	17	93
6*	$(CH_3S)_2Hg$	0.5 g.	H_2	„	17 Tage	4	22
7*	—	—	O_2	„	1 Monat	4	22
8	—	—	H_2	„	„	0	0
9*	$(CH_3S)_2Hg$	0.5 g.	Luft	„	17 Tage	10	55
10	$(CH_3S)_2Hg$	0.5 g.	H_2	„	1 Monat	6	33
11	—	—	O_2	„	„	11	61

Mit * versehene Experimente wurden in der Dunkelkammer, die übriger bei diffusem Licht ausgeführt.

Die Katalytische Wirkung des Sauerstoffs wird durch Beleuchtung sehr verstärkt. Licht allein ohne Sauerstoff übt aber keinen Einfluss auf die obige Anlagerungsreaktion aus.

Chemisches Institut
der Kaiserlichen Universität
zu Osaka.

(3) Y. Urushibara und M. Takebayashi, dies Bulletin, **11** (1936), 798; **12** (1937), 138, 173.

On the Nature of Foam. III. The Foam Formation of Ternary System, Acetic Acid—Benzene—Water.

By Tunetaka SASAKI.

(Received December 14, 1938.)

The foam formation of the ternary system of acetic acid–ethyl ether–water (AEW) was reported and some explanations were given in the preceding paper.[1] It was further confirmed that the ternary system of acetic acid–benzene–water (ABW) shows a similar behaviour in the foam formation to the system of AEW. The present paper describes the investigation of the foam formation of the ternary liquid system of ABW.

Experimental Procedure. In the ternary system or ABW, benzene is insoluble in water, while acetic acid is soluble in all proportions both in water and in benezene. The mutual solubility curve and tie-lines of this system are obtained by the same methods as were described in the preceding paper,[1] and the data of which are given in Tables 1 and 2, respectively. These data are depicted in Fig. 1. To draw tie-lines, we take one point corresponding to the composition given in Table 2, which is situated in the heterogeneous region of Fig. 1, and draw a straight line so as its section made by the mutual solubility curve is divided at that point in two portions, the ratio of which being equal to that of corresponding volumes of upper and lower layers shown in Table 2.

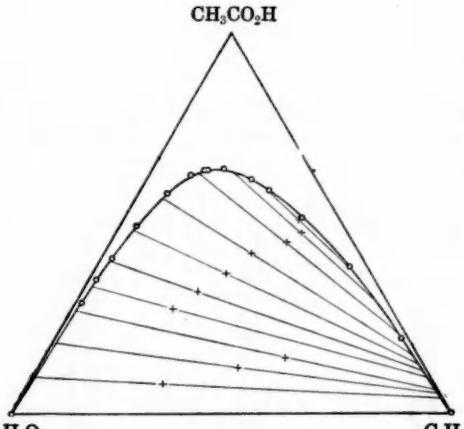

Fig. 1.

Measurements of the foam formation were then undertaken by means of the shaking apparatus in the same manner as was described in the preceding paper.[1] Thus the foam height H and the stability S have been measured after ten seconds' shaking of a solution with the frequency of 300 vibrations per minute at about 20°C.

Experimental Results. The results of measurements are shown in Table 3.[2] Here, the product of S and H is considered to be the measure of the foam formation. Fig. 2 shows the diagram which represents the relation between composition and foam formation of ABW-system.

(1) Sasaki, this Bulletin, **13** (1938), 669.
(2) Only a part of the data are shown for the economy of spaces.

Table 1.

Volume ratio of limiting turbid mixture (about 20°)		
Acetic acid	Benzene	Water
0	0	10.00
1.98	7.90	0.12
2.92	0.14	6.94
3.53	0.17	6.30
3.85	5.77	0.38
4.10	0.23	5.67
4.93	0.38	4.69
5.15	4.04	0.81
5.80	0.65	3.55
5.89	2.93	1.18
6.17	2.39	1.44
6 28	0.93	2.77
6.40	1.20	2.40
6.41	2.05	1.64
6.42	1.63	1.95
0	10.00	0

Table 2.

Composition in volume ratio			Volume ratio	
Acetic acid	Ben-zene	Water	upper layer	lower layer
5.10	4.00	0.90	0.625	1.000
4.74	4.21	1.05	0.920	1.000
4.50	4.00	1.50	0.785	1.000
4.21	3.44	2.35	0.578	1.000
3.71	3.05	3.24	0.486	1.000
3.21	2.62	4.17	0.385	1.000
2.80	2.30	4.90	0.322	1.000
1.50	5.50	3.00	1.381	1.000
1.23	4.53	4.24	0.907	1.000
0.82	3.02	6.16	0.452	1.000

Table 3.

Composition in volume ratio			Height of foam, H(cm.)	Stability of foam, S(second)	Degree of foam formation, S-H
Acetic acid	Benzene	Water			
0	1.50	8.50	0	0	0
0	2.63	7.37	0	0	0
0.04	4.98	4.98	0	0	0
0.33	5.92	3.75	0	0	0
0.50	0	9.50	2.2	12.5	27.5
0.50	0.80	8.70	3.1	7.0	21.7
0.50	2.00	7.50	2.6	5.9	15.3
0.50	5.00	4.50	1.1	5.1	5.6
0.80	0	9.20	2.2	13.5	29.7
0.80	3.40	5.80	1.4	4.6	64.4
1.00	0	9.00	2.3	15.0	34.5
1.00	1.30	7.70	1.6	7.1	11.4
1.00	2.50	6.50	1.4	4.9	6.9
1.00	4.50	4.50	0.7	2.6	1.8
1.10	4.90	4.00	0	0	0
1.20	0	8.80	2.2	12.6	27.7
1.48	0.10	8.42	1.7	5.8	9.9
1.50	0	8.50	2.5	12.6	31.5
1.50	3.20	5.30	0.6	1.8	1.1
1.60	0.70	7.70	1.4	4.8	6.7
1.95	3.42	4.63	0	0	0
1.98	7.90	0.11	0	0	0
2.00	0	8.00	1.9	9.7	18.4
2.00	1.30	6.70	0.8	3.1	2.5
2.50	1.25	6.25	0	0	0
3.00	0.47	6.53	0	0	0
3.49	1.78	4.73	0	0	0
3.50	0	6.50	1.9	3.0	5.7
3.80	5.90	0.30	0	0	0
4.50	5.00	0.50	1.2	1.5	1.8
4.82	0.38	4.80	0	0	0
4.90	2.50	2.60	0	0	0
4.90	4.32	0.78	1.9	8.4	16.0

Table 3.—(*Concluded*)

Composition in volume ratio			Height of foam, H(cm.)	Stability of foam, S(second)	Degree of foam formation, $S \cdot H$
Acetic acid	Benzene	Water			
5.00	4.40	0.60	1.1	1.4	1.5
5.17	3.90	0.95	0	0	0
5.22	3.94	0.84	1.6	4.9	7.8
5.30	4.00	0.70	1.2	1.8	2.2
5.32	4.68	0	0	0	0
5.90	3.00	1.10	2.0	6.9	13.8
6.00	3.00	1.00	1.6	2.3	3.7
6.15	0.87	2.98	0	0	0
6.32	1.96	1.72	0	0	0
6.48	1.33	2.19	1.6	1.9	3.0
6.50	2.00	1.50	0.8	2.1	1.7
7.00	0	3.00	1.0	1.3	1.3
7.00	1.50	1.50	1.0	1.3	1.3

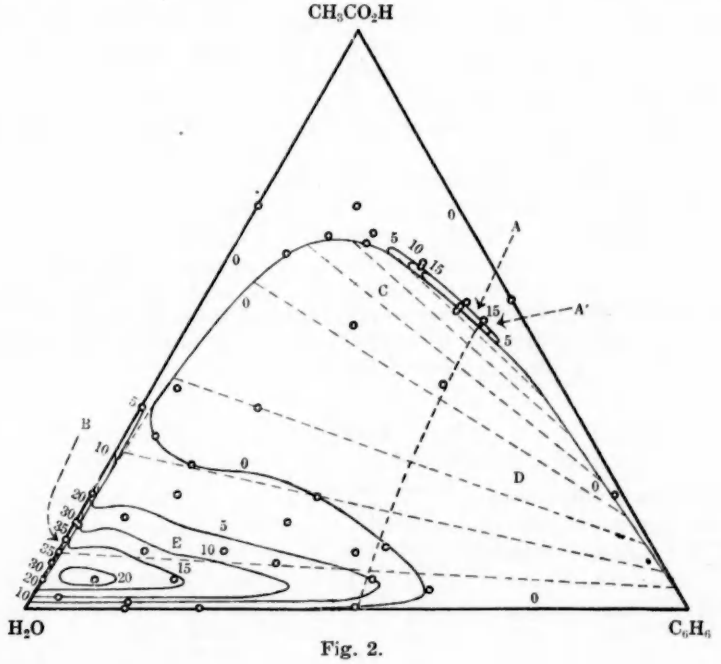

Fig. 2.

Discussion. The diagram of the foam formation of ABW-system, like that of AEW-system, is separated into two regions by the mutual solubility curve, that is homogeneous and heterogeneous regions.

(1) *Homogeneous region.* The surface of the diagram has two maxima of foam formation along the mutual solubility curve at the vicinity of the points A and B in Fig. 2, respectively. The other portions of the

homogeneous region can froth more or less. In this region, the shape of surface of the diagram, as a whole, is analogous to that of AEW-system, and the maximum near the point B is explained from its position being close to the composition of maximum foam formation in the binary system of acetic acid–water, as in the case of AEW-system. In the case of ABW-system, however, homogeneous region near the point B is so narrow that the diagram of this part is composed of two steep surfaces forming a sharp edge as shown in Fig. 2.

The foam formation also shows its maximum near the point A in Fig. 2, but it is less exaggerated in this system than in AEW-system and the height of maximum near the point A is even smaller than that near the point B in ABW-system. The explanation was made in the preceding paper[1] upon the foam formation of the system near the point A, referring to the analogous phenomena of opalescence and anomalous viscosity exhibited by the ternary system of benzene–ethyl alcohol–water, as due to its liability to form emulsion.

In the present case, the conditions are more favourable for this explanation, because the opalescent zone of benzene–ethyl alcohol–water system and the region A in Fig. 2 coincide each other and they are both situated in the vicinity of the point of intersection made by the mutual solubility curve and the locus of middle points of tie-lines (A′ in Fig. 2.). We can explain, therefore, the maximum of foam formation, the critical opalescence and the anormalous viscosity from the colloidal behaviour of corresponding systems.

(2) *Heterogeneous region.* Heterogeneous region may be divided into three parts, namely, region C, D and E in Fig. 2.

(a) Region C. In the system of this region, an upper layer consisting of water, acetic acid and excessive benzene is smaller in volume compared with a lower one consisting of acetic acid, benzene and excessive water, while the surface tension of the former is smaller than that of the latter but not so markedly as in the system of E region. These relations are shown in the sixth column of Table 4.

Table 4.

Composition in volume ratio			Surface tension (relative)		Foam formation	
Acetic acid	Benzene	Water	upper layer	lower layer	$V^* < V_l$	$V_u > V_l$
4.83	3.92	1.25	0.402	0.421	C region in Fig 2, non foamy.	D region in Fig. 2, non foamy.
4.31	3.54	2.15	0.416	0.465		
2.42	4.35	3.23	0.421	0.553		
1.26	5.04	3.70	0.416	0.651	E region in Fig. 2, remarkably foamy. (three layered film)	
0.74	2.72	6.53	0.407	0.740		
0	5.00	5.00	0.419	0.999		

* V_u and V_l denote volumes of upper and lower liquids respectively, coexisting in the corresponding heterogeneous system.

When we shake a system of this region, the film of air bubble produced in the liquid becomes heterogeneous and the foam cannot be produced[3] as in the corresponding case of AEW-system.

(b) Region D. This corresponds to the heterogeneous region, the lower layer of which, consisting of acetic acid, benzene and excessive water and having a smaller volume, is dispersed in an upper one consisting of acetic acid, water and excessive benzene. The last column of Table 4 corresponds to this region.

In such system, certain degree of foam formation can be expected on shaking, because emulsion droplets of larger surface tension than the dispersing medium do not interfere with the foam produced in this system as was observed in AEW-system. But in the mixture corresponding to this region of ABW-system, practically no foam can be produced on shaking. It is perhaps because the upper layer of this system does not foam while that of AEW-system foams a little.

(c) Region E. In the heterogeneous system belonging to this region, the upper layer consisting of acetic acid, water and excessive benzene is smaller in volume and markedly smaller in surface tension than the lower one consisting of acetic acid, benzene and excessive water, as shown in the sixth column of Table 4.

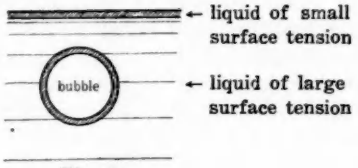

Fig. 3a.

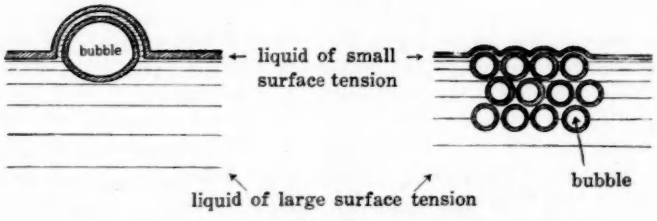

Fig. 3b.

In ABW-system of this region, the upper layer is dispersed in the lower one on shaking. At the same time, air bubbles are also produced both in emulsion droplets and in the dispersing medium, but bubbles in the dispersing medium readily and entirely go into the interior of the emulsion droplets on account of the large difference in surface tension between both layers. Thus, air bubbles are covered with homogeneous films made of emulsion droplets which are again surrounded by the dispersing medium. These circumstances are readily understood from Fig. 3a, as in the case of the corresponding system of AEW.[1]

Such air bubbles go up to and accumulate at the interface of benzene–water, and produce the foam as shown in Fig. 3b. Now, the foam is

(3) Sasaki, this Bulletin, **11** (1936), 797.

covered at least by three layers of homogeneous films, of which middle layer is an aqueous mixture of larger surface tension than the outer ones. Therefore, air in bubbles cannot escape towards outside on account of the difficulty in breaking the innermost films (i.e. exposing itself to the middle layer). In other words, the foam is stabilised in such systems.

Although mere emulsion drops containing air bubbles were observed in AEW-system of this region, fairly stable foam is produced in the case of ABW-system. In Fig. 2, relatively larger zone of remarkable foam formation can be seen in the region E. It will be emphasized that these foams, consisting of triple layered films, are entirely different in its nature from the ordinary foams covered with single homogeneous film.

In region E of ABW-system, surface constituting the diagram is steep along the straight line connecting the vertices of benzene and water. This means that a heterogeneous mixture of water and benzene foams considerably by the addition of small quantity of acetic acid. Such phenomenon can also be observed when we substitute benzene for liquid aliphatic hydrocarbon such as hexane. This suggests an interesting practical application of detecting trace of surface active substances usually existing as impurities in hexane or its homologues. Namely, when we shake water with a relatively small volume of hexane which was obtained by the usual method of repeated distillation from commercial products, foam formation may be observed. No foam can be produced, however, in the mixture of water and hexane from which traces of impurities are carefully removed by shaking it for a long time with fuming sulphuric acid and distilling.[4] This is explained from the fact that the impurities mainly consist of surface active substances and behave just like acetic acid in the case of ABW-system.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed by a grant given to Prof. Sameshima from Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

Summary.

(1) The foam formation of liquid ternary system of acetic acid–benzene–water (ABW) has been measured by means of a shaking apparatus, and a diagram has been drawn between the degree of foam formation and the composition.

(2) The foam formation of homogeneous system of ABW is analogous to that of acetic acid–ethyl ether–water (AEW), showing two maxima of foam formation. In the heterogeneous system of ABW, however, remarkable foam formation can be observed, instead of mere emulsion droplets containing bubbles in the case of AEW-system.

(3) The explanation of foam formation in heterogeneous ABW-system has been attempted.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(4) A. Weissberger and E. Proskauer, "Organic Solvents," 99, (1935).

Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. IV. Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche der Oxyde von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel.[1]

Von Noriyoshi MORITA, Haruo TANAKA und Toshizo TITANI.

(Eingegangen am 26. Dezember 1938.)

Inhaltsübersicht. Unter Verwendung der Oxyde der zur vierten Hauptreihe des periodischen Systems gehörigen Elemente, nämlich der Oxyde von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel als Katalysator wird die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und an schwerem Sauerstoff angereichertem Wasserdampf untersucht. Misst man die katalytische Wirksamkeit eines bestimmten Oxyds durch die Temperatur, wo die Austauschreaktion an seiner Oberfläche erst bemerkbar wird, so findet man, dass sie sich mit zunehmender Gruppennummer periodisch verändert. Am stärksten wirksam ist das Manganoxyd, am schwächsten dagegen das Titanoxyd, und die Oxyde der anderen Elemente ordnen sich betreffend ihrer katalytischen Wirksamkeit zwischen diesen beiden Extremen.

Einleitung und Versuchsanordnung. Seit letztem Jahr beschäftigen wir uns mit dem Versuch über die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und sauerstoffhaltigen Verbindungen, hauptsächlich Wasserdampf, an der Oberfläche der Oxyde der verschiedenen Arten der Elemente. Während dieses Versuches fanden wir, dass es eine gewisse Regelmässigkeit zwischen der katalytischen Wirksamkeit des Oxyds eines bestimmten Elements und dem Platz gibt, den das betreffende Element im periodischen System einnimmt. Als ein schönes Beispiel dafür teilen wir hier die Versuche mit, die wir mit den Oxyden der zur vierten Hauptreihe gehörigen Elemente, nämlich mit den Oxyden von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel, ausgeführt haben. Die Versuchsmethode und -anordnung, die wir dabei benutzt haben, ist im grossen und ganzen dieselbe wie die in I. Mitteil. beschrieben wurde. Deshalb wird jede Einzelheit auf dort verwiesen und hier sollen nur die Darstellungsmethode der zum Versuch verwendeten Oxyde und die damit gewonnenen Versuchsergebnisse mitgeteilt werden.

Darstellung der Oxyde. Calciumoxyd CaO—Käufliches reines Calciumoxyd wird zunächst sorgfältig zerkleinert und dann im Porzellantiegel bis auf ca. 900°C. etwa vier Stunden lang erhitzt.

Titanoxyd TiO_2—Pulveriges reines Titanoxyd aus dem Handel wird in verdünnter Salzsäure einige Stunden lang erwärmt und dann mit destilliertem Wasser so lange gewaschen, bis keine Chlorionen im Filtrat mehr nachgewiesen werden können. Das so gereinigte Oxyd wird im Luftbad gut getrocknet und zum Schluss im Porzellantiegel bis auf etwa 800°C. einige Stunden lang erhitzt.

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(1) I. Mitteil.: Dies Bulletin, **13** (1938), 357; II. Mitteil. *ibid.*, **13** (1938), 601; III Mitteil.: *ibid.*, **13** (1938), 656.

Vanadinoxyd V_2O_5—Reines Ammoniumvanadat aus dem Handel wird im Porzellantiegel sorgfältig erhitzt. Das dadurch gewonnene Vanadinpentoxyd wird aber durch die weitere Erhitzung bis auf einige Grade über seinen Schmelzpunkt (658°C.) vollkommen geschmolzen und nach der Abkühlung wird das Geschmolzene zu kleinen Körnchen zerkleinert.

Chromoxyd Cr_2O_3—Der Niederschlag von Chromhydroxyd, der sich beim Versetzen der wässrigen Lösung von reinem Chrom(III)-nitrat mit verdünnter Ammoniaklösung abgeschieden hat, wird zunächst mit destilliertem Wasser gründlich gewaschen, dann im Luftbad getrocknet und zum Schluss durch die Erhitzung im Porzellantiegel bis auf etwa 600°C. restlos bis zum Oxyd entwässert. Das so gewonnene Oxyd wird aber vor dem Gebrauch wieder bis auf 700°C. im Sauerstoffstrom einige Stunden lang erhitzt.

Manganoxyd Mn_3O_4—Die wässrige Lösung von reinem Mangan(II)-chlorid wird mit Natriumcarbonat versetzt und das dabei abgeschiedene Mangancarbonat, nachdem es mit destilliertem Wasser gründlich gewaschen worden ist, im Luftbad gut getrocknet. Das so gewonnene Carbonat wird dann im Sauerstoffstrom über Nacht lang sorgfältig erhitzt, bis es sich vollkommen in Oxyd verwandelt hat. Deshalb dürfte es die Zusammensetzung von Mn_3O_4 besitzen.

Eisenoxyd Fe_2O_3—Der Niederschlag von Eisenoxydhydrat, der sich bei der Versetzung der wässrigen Lösung von „Eisennitrat, krist." aus Kahlbaum mit Ammoniakwasser abgeschieden hat, wird mit heissem Wasser mehrmals gewaschen und im Luftbad getrocknet. Dann wird er durch die etwa einstündige Erhitzung im Porzellantiegel bis auf ca. 800°C. vollkommen bis zum Oxyd zersetzt.

Nickeloxyd NiO—Der Niederschlag von Nickeloxydhydrat, der durch die Versetzung der wässrigen Lösung des reinen Nickelsulfats mit Ätznatron hergestellt worden ist, wird mit destilliertem Wasser so lange gewaschen, bis keine Sulfationen im Filtrat mehr nachgewiesen werden können. Dann wird er im Luftbad getrocknet und zum Schluss im Porzellantiegel bis auf ca. 800°C. eine Stunde lang erhitzt.

Versuchsergebnisse. Die Ergebnisse der Austauschversuche, die unter Benutzung der oben beschriebenen Arten der Oxyde ausgeführt wurden, sind in folgenden Tabellen 1 bis 7 zusammengestellt. In diesen Tabellen besitzen die einzelnen Buchstaben bzw. Abkürzungen folgende Bedeutungen:

Δs_a und Δs_e: der gewöhnlichem Wasser gegenüber gemessene Dichteüberschuss des zum Versuch benutzten an schwerem Sauerstoff angereicherten schweren Wassers und zwar Δs_a der Dichteüberschuss vor dem Versuch, dagegen Δs_e der nach dem Versuch.

$\Delta s_a(O)$: solch ein Anteil des gesamten und anfänglichen Dichteüberschusses (Δs_a) des schweren Wassers, der lediglich auf die Anreicherung der schweren Sauerstoffisotope zurückgeführt werden kann.

$\%A$: diese Quantität, die weiter unten das „prozentuale Austauschmass" benannt werden soll, stellt das prozentuale Verhältnis der wirklich gefundenen Abnahme der Dichte des schweren Wassers, nämlich $\Delta s_a - \Delta s_e$, gegen den theoretischen Wert dar, der sich beim vollständigen Austausch ergeben würde. Dieser letztere Wert kann aber mit Hilfe des

Mengenverhältnisses des zum Versuch verwendeten gasförmigen Sauerstoffs und des Wasserdampfes sowie von Δs_a und $\Delta s_a(O)$ leicht errechnet werden (vgl. I. Mitteil.).

M: Menge des zum Versuch verwendeten Oxyds in g.

Das bei jedem Versuch in der vorliegenden Arbeit verwendete Reaktionsgasgemisch aus Sauerstoff und Wasserdampf bestizt, ebenso wie bei den Versuchen in I. Mitteil., die Zusammensetzung von $O_2:H_2O = 2:1$, und die in der ersten Spalte der Tabellen angegebene Versuchsnr. zeigt die zeitliche Reihenfolge der einzelnen Versuche.

Tabelle 1. Calciumoxyd. $\Delta s_a = 41.6\,\gamma$, $\Delta s_a(O) = 26.1\,\gamma$, $M = 8\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
5	350	40.0	1.6	7
6	420	38.6	3.0	14
2	510	31.1	10.5	47
4	560	20.6	21.0	95
1	610	18.4	23.2	104
3	690	19.4	22.2	100

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

Tabelle 2. Titanoxyd. $\Delta s_a = 41.6\,\gamma$, $\Delta s_a(O) = 26.1\,\gamma$, $M = 9\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
2	510	40.5	1.1	5
5	530	40.3	1.3	6
1	600	38.5	3.1	14
4	650	37.9	3.7	17
3	690	31.3	10.3	46
6	790	20.5	21.1	95

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

Tabelle 3. Vanadinoxyd. $\Delta s_a = 31.3\,\gamma$, $\Delta s_a(O) = 19.5\,\gamma$, $M = 10\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
2	380	30.5	0.8	5
3	460	30.2	1.1	7
1	540	29.2	2.1	12
4	600	26.3	5.0	30
—	658 (Schmp.)		—	—

$$\% A = \frac{\Delta s_a - \Delta s_e}{16.9} \times 100$$

Tabelle 4. Chromoxyd. $\Delta s_a = 36.8\,\gamma$, $\Delta s_a(O) = 22.8\,\gamma$, $M = 7\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
5	380	34.8	2.0	10
4	410	33.9	2.9	15
2	460	24.6	12.2	62
3	510	16.2	20.6	106
1	540	16.6	20.2	104

$$\% A = \frac{\Delta s_a - \Delta s_e}{19.5} \times 100$$

Tabelle 5. Manganoxyd.[2] $\Delta s_a = 33.5\,\gamma$, $\Delta s_a(O) = 23.1\,\gamma$, $M = 11\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
7	210	35.5	0.0	0
8	250	35.5	0.0	0
6	300	26.5	9.0	45
4	350	20.0	15.5	78
3	400	17.1	18.4	93
2	450	17.2	18.3	92
5	500	16.7	18.8	95
1	550	15.1	20.4	103

$$\% A = \frac{\Delta s_a - \Delta s_e}{19.8} \times 100$$

Tabelle 6. Eisenoxyd. $\Delta s_a = 41.6\,\gamma$, $\Delta s_a(O) = 26.1\,\gamma$, $M = 15\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
7	400	40.6	1.0	4
5	450	37.4	4.2	19
2	500	34.6	7.0	32
6	550	31.1	10.5	47
4	600	24.8	16.8	76
1	680	18.1	23.5	106
3	760	17.8	23.8	107

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

(2) Dieser Versuch wurde von Tanaka durchgeführt.

Tabelle 7. Nickeloxyd. $\Delta s_a = 41.6\,\gamma$, $\Delta s_a(O) = 26.1\,\gamma$, $M = 8\,g$.

Versuchsnr.	Temperatur °C.	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass % A
3	400	40.6	1.0	4
5	470	37.8	3.8	17
1	550	23.3	18.3	82
4	630	19.6	22.0	99
2	700	18.4	23.2	104
6	740	19.4	22.2	100

$$\% A = \frac{\Delta s_a - \Delta s_e}{22\,2} \times 100$$

Diskussion. Wenn man die in den oberen Tabellen 1 bis 7 angegebenen Werte von Austauschmass $\%A$ gegen die Versuchstemperatur einzeichnet, ergibt sich die Kurvengruppe, die in Abb. 1 wiedergegeben ist. Aus dieser Abb. ersieht man aber ohne weiteres, dass die katalytische Austauschreaktion der O-Atome zwischen gasförmigen Sauerstoff und Wasserdampf am leichtesten an der Oberfläche des Manganoxyds dagegen am schwersten an Titanoxyd stattfindet, während die anderen Oxyde betreffend ihrer katalytischen Wirksamkeit sich zwischen diesen beiden

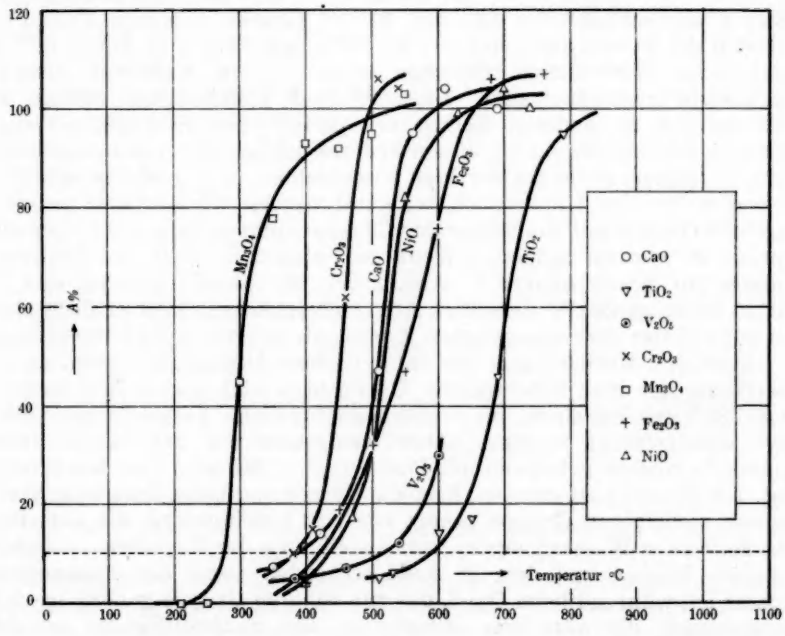


Abb. 1. Die Abhängigkeit des Austauschmasses % A von der Versuchstemperatur.

Extremen anordnen. Die Form u. a. die Neigung dieser Kurve hängt offenbar von manchen Faktoren ab, wie z.B. von der Menge, Beschaffenheit sowie der Korngrösse des benutzten Katalysators und weiter von der Strömungsgeschwindigkeit des reagierenden Gasgesmisches. Aber erstens weil die Strömungsgeschwindigkeit des Gasgemisches immer genau dieselbe war und die Menge sowie die Korngrösse der einzelnen Katalysatoren auch nicht viel von einander abwich und zweitens weil die Form der Kurven in Abb. 1 an ihrem unteren Ende durch diese Faktoren am wenigstens beeinflusst wird, darf man die katalytische Wirksamkeit jedes Katalysators in der ersten Annährung durch die Temperatur vergleichen, wo die Austauschreaktion an der Oberfläche des betreffenden Katalysators erst bemerkbar wird. Aus diesem Grunde wird aus der Kurvengruppe in Abb. 1 solch eine Temperatur $t(10\%)$ entnommen, wo das gefundene Austauschmass $\%A$ erst 10% beträgt. Wenn man nun die so gefundenen Werte von $t(10\%)$, die in der letzten Spalte der Tabelle 8 wiedergegeben sind, gegen die Nummer der Gruppe, zu der das Element jedes betreffenden Oxyds im periodischen System gehört, einzeichnet, dann erhält man die Kurve, die in der nebenstehenden Abb. 2 gezeigt wird. Bei dieser Einzeichnung tragen wir aber die Temperatur $t(10\%)$ in der Ordinate absichtlich von oben nach unten ein, um dadurch die Punkte der einzelnen Oxyde nach der Reihenfolge ihrer katalytischen Wirksamkeit von oben nach unten sich anordnen zu lassen. Diese Kurve zeigt, dass die katalytische Wirksamkeit des Oxyds sich mit der Gruppennummer im periodischen System ziemlich regelmässig und zwar periodisch verändert; am stärksten wirksam ist das zur siebenten Gruppe gehörige Manganoxyd, dagegen am schwächsten das zur vierten Gruppe gehörige Titanoxyd, während die zu den anderen Gruppen gehörigen Oxyde in Bezug auf die katalytische Wirksamkeit zwischen diesen beiden Extremen ziemlich regelmässig angeordnet sind. Diesähnliche Regelmässigkeit können wir auch bei den zu anderen Reihen des periodischen Systems gehörigen Elemente finden, obwohl bei diesen anderen Reihen das Versuchsmaterial nicht so lückenlos wie bei der hier untersuchten vierten Reihe erhältlich ist und weiter der Unterschied der katalytischen Wirksamkeit zwischen einzelnen Oxyden mit zunnehmender Gruppennummer immer weniger ausgeprägt zu werden scheint. Wenn wir aber z.B. statt des fehlenden Punktes für Scandiumoxyd in Abb. 2 den für Aluminiumoxyd, das zur dritten Reihe gehört, in derselben Abb. einzeichnen, so liegt er doch ziemlich gut auf der dort angegebenen Kurve, wie der viereckige Punkt zeigt.

Über den Mechanismus der katalytischen Austauschreaktion an der Oberfläche der hier untersuchten Oxyde lässt sich nicht ohne weiteres etwas Sicheres aussagen, bis weitere ausführliche Versuche mit jedem Oxyd durchgeführt werden. Aber wenigstens aus den bisher untersuchten Versuchsergebnissen mit Platin (vgl. I. Mitteil.) und Kupferoxyd (vgl. III. Mitteil.) zu urteilen, liegt die Vermutung nahe, dass beim Oxyd, das zur niedrigeren Gruppe gehört wie z.B. Calciumoxyd, die aktivierte Adsorption des Wasserdampfes bzw. die Bildung der Zwischenverbindung zwischen Wasser und dem in Rede stehenden Oxyd der massgebende Prozess ist, während beim Oxyd, das zur höheren Gruppe gehört, wie z.B. Manganoxyd, die aktivierte Adsorption des Sauerstoffgases an dem betreffenden Oxyd die massgebende Rolle spielt.

Tabelle 8. Vergleich der katalytischen Wirksamkeit der verschiedenen Oxyde.

Oxyde	Die zum Versuch benutzte Menge in g.	$t(10\%)$ °C.
CaO	8	390
TiO_2	9	590
V_2O_5	10	520
Cr_2O_3	7	380
Mn_3O_4	11	280
Fe_2O_3	15	420
NiO	8	430

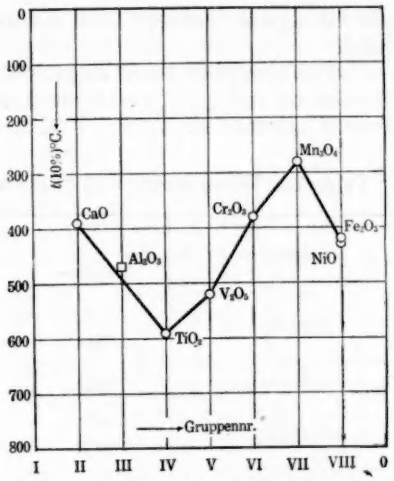


Abb. 2. Abhängigkeit der katalytischen Wirksamkeit der verschiedenen Oxyde von der Gruppennummer im periodischen System.

Zum Schluss möchten wir der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung zur Ausführung dieser Arbeit unseren wärmsten Dank aussprechen.

Physikalisch-chemisches Laboratorium
der Kaiserlichen Universität Osaka
und
Siomi-Institut für physikalische
und chemische Forschung.

The OH-Vibration Spectrum in the Photographic Infrared. II.

By San-ichiro MIZUSHIMA, Tutomu KUBOTA, and Yonezo MORINO.

(Received December 26, 1938).

In our previous work[1] we studied the near infrared absorption bands of monovalent alcohols and ortho-substituted phenols in the liquid state as well as in carbon tetrachloride solutions. The present paper deals with the investigation extended to the vapours of these substances. The experimental apparatus was essentially the same as that described in our

(1) Mizushima, Uehara, and Morino, this Bulletin, **12** (1937), 132.

previous paper, except that a three-meter absorption tube of glass was used.

The observed wave lengths of absorption maxima corresponding to the second and third overtones are shown, respectively, in the second and fourth columns of Table 1. Our values for the second overtone are in

Table 1. Wave length (Å) of absorption maxima of OH vibration bands.

Substance	ν_2		ν_3	
	Vapour	Solution	Vapour	Solution
CH_3OH	9473 9514	9593	7282 7311	7376
C_2H_5OH	9533	9621	7323	7411
n-C_3H_7OH	9510 9557	9626	7304 7353	7411
n-C_4H_9OH	9511 9557	9610	7308 7356	7430
HCOOH	9773 9815	— —	7513 7534	— —
CH_3COOH	9760	—	7501	—
C_2H_5COOH	9761	—	7502	—
C_6H_5OH	9564	9679	7345	7446
o-C_6H_4ClOH	9568 9812	9687 9907	7346 7569	7446 7621
o-C_6H_4BrOH	9564 9884	9682 9995	7346 —	7462 7710
C_2H_4ClOH	9486 9538 9646	9595 9726	7287 7334 7429	— — —

general in good agreement with those of Badger and Bauer,[2] Herzberg and Verleger,[3] and Naherniac,[4] so far as the comparison can be made. For methyl alcohol Badger and Bauer[5] carried out also high dispersion measurement in the region of the third overtone.

The two absorption maxima observed for some alcohols and acids probably belong to different branches of the same vibration band, while those for ortho-halogenated phenols which have much larger wave length differences correspond to different bands of the two molecular species

(2) Badger and Bauer, *J. Chem. Phys.*, **4** (1936), 711.
(3) Herzberg und Verleger, *Phyik. Z.*, **37** (1936), 444.
(4) Naherniac, *Ann. phys.*, **7** (1937), 528.
(5) Badger and Bauer, *J. Chem. Phys.*, **4** (1936), 469.

given by the quantum mechanical resonance[1][6][7] (see Fig. 1). Of the two absorption maxima observed for the latter substances, that having the wave-length nearly equal to that of phenol is assigned to configuration II of Fig. 1 in which the interaction between OH and Cl is much smaller than that expected in the alternative configuration. The relative number of molecules in configuration II is, however, much smaller than that expected from the intensity ratio of the said two absorption maxima, as was shown by our previous dipole measurement.[8] This is due to the interaction between the chlorine and the hydroxyl hydrogen which reduces the absorption intensity of OH vibration considerably. The wave lengths of absorption maxima found for acids are much longer than those for alcohols, which indicates that practically all the molecules of acids assume configuration I of Fig. 2. This results is in conformity with the conclusion from the dipole measurement.[9][10]

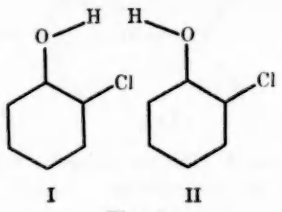


Fig. 1.

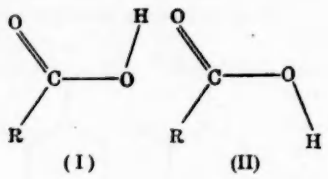
The absorption maxima observed for vapours have longer wave lengths by ca. 100 Å than those for the dilute carbon tetrachloride solutions[11] (third and fifth columns of Table 1). This fact is interesting when compared with the observation of Errera and Mollet[12] that for the fundamental tone the absorption maximum of the vapour of C_2H_5OH has practically the same wave length as that of the carbon tetrachloride solution. The effect of solvent molecule is, therefore, much larger for a higher quantum state than that for a lower one.

For ethylene chlorhydrin we observed three absorption maxima ($\nu_2^a = 9486$ Å, $\nu_2^b = 9538$ Å, $\nu_2^c = 9646$ Å) in the vapour state and two ($\nu_2^d = 9595$ Å, $\nu_2^e = 9726$ Å) in dilute carbon tetrachloride solutions. From the experimental results obtained for the other substances shown in Table 1, it may be considered that ν_2^a and ν_2^b correspond to ν_2^d and ν_2^c to ν_2^e. It is possible that these two absorption regions of ethylene chlorhydrin may have an explanation similar to that applied to the ortho-halogenated phenols. From the observed values of dipole moment[13] it

(6) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464; Wulf, Liddel, and Hendricks, *ibid.*, **58** (1936), 2287.
(7) Pauling, *J. Am. Chem. Soc.*, **58** (1936), 94.
(8) Kozima and Mizushima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **31** (1937), 296.
(9) Zahn, *Phys. Rev.*, **37** (1931), 1516; *Trans. Faraday Soc.*, **30** (1934), 804.
(10) Mizushima, *J. Chem. Soc. Japan*, **57** (1936), 936.
(11) In our previous communication we calculated the frequency of infinitesimal vibration ω and the anharmonicity factor x from our experimental values for the second and third overtones, putting the vibrational level of the quantum number v as

$$G(v) = \omega\left(v+\frac{1}{2}\right) - x\omega\left(v+\frac{1}{2}\right)^2$$

Using ω and x thus obtained we can calculate the frequencies of the fundamental tone and first overtone for C_2H_5OH as 3648 cm.$^{-1}$ and 7114 cm.$^{-1}$ respectively, both of which are in good agreement with the experimental values of Errera and Mollet (3640 cm.$^{-1}$) and Wulf and Liddel (7090 cm.$^{-1}$).
(12) Errera and Mollet, *Nature*, **138** (1936), 882; *Compt. rend.*, **204** (1937), 259.
(13) Zahn, *Physik. Z.*, **33** (1932), 525.



(I) (II)

Fig. 2. The two molecular configurations of carboxylic acids expected from the quantum mechanical resonance.

Table 2. Wave length variation of absorption maximum of ethylene chlorhydrin with concentration.

1 : x*	Wave length (Å) of absorption maximum.	
pure liquid	9760	—
1 : 1	9755	—
1 : 4	9731	—
1 : 8	9724	9621
1 : 16	9724	9616
1 : 80	9725	9609
1 : 300	9726	9595
vapour	9646	9538, 9486

* The solution consists of one part by volume of ethylen chlorhydrin and x parts of carbon terachloride.

is concluded that the molecular configuration of ethylene chlorhydrin corresponds either to the trans form $\overset{Cl}{\diagdown}CH_2-CH_2\overset{OH}{\diagup}$ or to the cis form $Cl\diagdown CH_2-CH_2\diagup OH$, but it is not unreasonable to assume the coexistence of these two forms, since the change in abundance ratio does not affect the apparent value of dipole moment. Then ν_2^a and ν_2^b (ν_2^d in solution) can be assigned to the trans form and ν_2^c (ν_2^e in solution) to the cis form, as the former will have wave lengths not much different from those of alcohols owing to the smaller interaction between Cl and OH. This assignment is in conformity with the behaviours of these bands in carbon tetrachloride solutions as stated in the following (see Table 2). In the liquid state and in concentrated solutions we observed a broad band around $\lambda = 9760$ Å, which on dilution becomes sharper and is shifted towards higher frequency region until the absorption maximum attains the wave length of 9726 Å, i.e. ν_2^c of the cis form. From a certain dilution on there appears in the shorter wave length region another band, which we have assigned to the trans form (ν_2^d). In other words the OH vibration of the cis form can be observed in all the conditions mentioned above, while that of the trans form only in the dilute solutions and in the vapour. This fact is just what we would expect from the configurations of these two molecular species, since the trans form will easily form *intermolecular* hydrogen bond (such as in the case of alcohols)[14] and therefore the OH vibration of a single molecule can hardly be observed in concentrated solutions, while there is much less probability for such bonding for the cis form whose hydroxyl hydrogen is coupled with the chlorine in the same molecule.

We are indebted to Hattori-Hôkôkai and Ôji-Seishi-Kaisha for grants in aid of this research.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

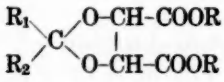
(14) According to Errera and Mollet[12] the OH band due to the isolated molecule of ethyl alcohol can be observed only in dilute solutions.

Synthesis of Cyclic Derivatives of Tartaric Acid by Condensing Alkyl *d*-Tartrates with Aliphatic Ketones. (Optical Activity and Chemical Structure in Tartaric Acid. V.*)

By Yojiro TSUZUKI.

(Received December 27, 1938.)

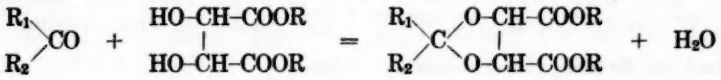
It was reported in the previous communications[1] that various cyclic derivatives of tartaric acid having the constitution



(I)

were synthesized by condensing alkyl *d*-tartrates with some aliphatic aldehydes and ketones as well as with alicyclic ketones. These compounds are suitable materials for the study of the relation between optical activity and chemical structure of tartaric acid, since they are all liquid compounds showing high lævo-rotation and exhibiting simple rotatory dispersion. And, indeed, the author has shown that the groups R_1, R_2 and R exert a certain definite effect on the optical rotatory power of the condensation products, in good agreement with the requirement of the molecular theories of de Mallemann[2] as well as of Boys.[3]

The purpose of the present work is to amplify the materials by condensing alkyl *d*-tartrates with a series of aliphatic ketones, in order to observe how the substituents R_1, R_2 and R influence the optical activity of the resulting compounds.



The following condensations were carried out: ethyl *d*-tartrate with methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl amyl ketone, dipropyl ketone and with methyl nonyl ketone, and in addition to these, methyl ethyl ketone with methyl *d*-tartrate, propyl *d*-tartrate and with isopropyl *d*-tartrate. The method of condensation was almost the same as in the cases of alicyclic ketones with ethyl *d*-tartrate[4] using also in this case phosphorus pentoxide as the condensation reagent. It is, however, to be noted that in the cases of symmetrical ketones, the temperature of the reaction must be lower and the duration of the reaction must accordingly be longer than in the cases of unsymmetrical ketones.

* Paper IV, this Bulletin, **12** (1937), 487.

(1) Y. Tsuzuki, this Bulletin, **10** (1935), 255; **11** (1936), 362; **11** (1936), 586; **12** (1937), 487.

(2) R. de Mallemann, *Trans. Faraday Soc.*, **26** (1930), 281.

(3) F. S. Boys, *Proc. Roy. Soc.* (London), A, **144** (1934), 655.

(4) Y. Tsuzuki, this Bulletin, **12** (1937), 487.

The condensation proceeds very smoothly in every case. The yield is fairly good, being 30–50% of the theoretical amount. The purification of the product is carried out in the same way as before, i.e. by evaporating off unchanged ketone and by dissolving out unchanged alkyl tartrate with aqueous borax. In the cases of propyl and isopropyl tartrates the purification is somewhat difficult, since these tartrates are not so easily soluble in borate; in these cases the above process of purification must be repeatedly performed, whereby the yield was somewhat impoverished.

The condensation products thus obtained and purified are transparent colourless liquids, showing strong lævo-rotation. Optical rotatory powers have also been measured in ethyl alcohol, in benzene and in cyclohexane. The optical activity and its solvent effect will be discussed in the following paper.

Ethyl methylethylmethylene-*d*-tartrate.

$C_{12}H_{20}O_6$ (260.16). (I) $R_1 = CH_3$, $R_2 = C_2H_5$, $R = C_2H_5$

To a mixture of 15 g. ethyl *d*-tartrate and 15 g. methyl ethyl ketone (Takeda's product, fractionated, b.p. 78.3–79°) was added 8 g. phosphorus pentoxide in portions at 70° during a period of 30 minutes. The liquid coloured pale yellow and the phosphorus pentoxide deeply brownish red. After the whole of phosphorus pentoxide was added, the mixture was maintained at this temperature for 30 minutes, and after cooling, the reaction product was extracted with ether. The ethereal solution was washed several times with a saturated solution of borax to remove unchanged ethyl *d*-tartrate and was finally dried over anhydrous sodium sulphate. After evaporating off the ether, the product was purified by fractional distillation in vacuo. Colourless liquid. Yield 8.5 g. Boiling point 158° (17 mm.), n_D^{20} 1.4361, d_4^{20} 1.0973, M_D 61.99 (62.01), $[\alpha]_D^{20}$ −35.02°, $[M]_D^{20}$ −91.10°. $[\alpha]_D^{20}$ −36.0° (in ethyl alcohol, 4.45%), $[M]_D^{20}$ −91.5° (in ethyl alcohol). $[\alpha]_D^{20}$ −40.2° (in benzene, 5.232%), $[M]_D^{20}$ −104.6° (in benzene). $[\alpha]_D^{20}$ −31.62° (in cyclohexane, 3.265%), $[M]_D^{20}$ −82.25° (in cyclohexane).

Ethyl methylpropylmethylene-*d*-tartrate.

$C_{13}H_{22}O_6$ (274.18). (I) $R_1 = CH_3$, $R_2 = C_3H_7$, $R = C_2H_5$

Ethyl *d*-tartrate (21 g.) and 13 g. methyl propyl ketone (Takeda's product, fractionated, b.p. 100–102°) gave 9 g. pure product. Colourless liquid boiling at 167.5° (20 mm.). n_D^{20} 1.4370, d_4^{20} 1.0770, M_D 66.69 (66.62), $[\alpha]_D^{20}$ −32.05°, $[M]_D^{20}$ −87.88°. $[\alpha]_D^{20}$ −31.8° (in ethyl alcohol, 5.400%), $[M]_D^{20}$ −87.2° (in ethyl alcohol). $[\alpha]_D^{20}$ −36.4° (in benzene, 5.534%), $[M]_D^{20}$ −99.8° (in benzene). $[\alpha]_D^{20}$ −28.86° (in cyclohexane, 3.611%), $[M]_D^{20}$ −79.14° (in cyclohexane).

Ethyl diethylmethylene-*d*-tartrate.

$C_{13}H_{22}O_6$ (274.18). (I) $R_1 = R_2 = C_2H_5$, $R = C_2H_5$

Ethyl *d*-tartrate (21 g.) and 13 g. diethyl ketone (Takeda's product, fractionated, b.p. 100–102°) gave 10.5 g. pure condensation product, when 20 g. P_2O_5 was added to the mixture at 60–70° during 50 minutes. Almost colourless liquid boiling at 169° (22 mm.). n_D^{20} 1.4390, d_4^{20} 1.0850, M_D 66.45 (66.62), $[\alpha]_D^{20}$ −23.06°, $[M]_D^{20}$ −63.23°. $[\alpha]_D^{20}$ −25.3° (in ethyl alcohol, 4.854%),

$[M]_D^{20}$ −69.4° (in ethyl alcohol). $[\alpha]_D^{20}$ −33.0° (in benzene, 5.108%), $[M]_D^{20}$ −90.5° (in benzene). $[\alpha]_D^{20}$ −20.89° (in cyclohexane, 3.631%), $[M]_D^{20}$ −57.27° (in cyclohexane).

Ethyl methylamylmethylene-*d*-tartrate.

$C_{15}H_{26}O_6$ (302.21). (I) $R_1 = CH_3$, $R_2 = C_5H_{11}$, $R = C_2H_5$

To a mixture of 12.6 g. ethyl *d*-tartrate and 7 g. methyl amyl ketone (Takeda's product, fractionated, b.p. 148°) was added 13 g. phosphorus pentoxide at 80–90°, during a period of 50 minutes, and heating was continued for one hour to maintain this temperature. Yield 8 g. Colourless liquid boiling at 180° (15 mm.), n_D^{20} 1.4399, d_4^{20} 1,0478, M_D 76.00 (75.87), $[\alpha]_D^{20}$ −26.59°, $[M]_D^{20}$ −80.36°. $[\alpha]_D^{20}$ −27.33° (in ethyl alcohol, 6.917%), $[M]_D^{20}$ −82.6° (in ethyl alcohol). $[\alpha]_D^{20}$ −31.13° (in benzene, 4.7656%), $[M]_D^{20}$ −94.1° (in benzene). $[\alpha]_D^{20}$ −24.19° (in cyclohexane, 4.2583%), $[M]_D^{20}$ −73.10° (in cyclohexane).

Ethyl dipropylmethylene-*d*-tartrate.

$C_{15}H_{26}O_6$ (302.21). (I) $R_1 = R_2 = C_3H_7$, $R = C_2H_5$

To a mixture of 15 g. ethyl *d*-tartrate and 8.3 g. di-*n*-propyl ketone (prepared from *n*-butyric acid by passing it over ThO_2 at 380–480°, b.p. 142–144°) was added 15 g. P_2O_5 at 80–90°. Yield 6 g. Pure colourless liquid boiling at 175°(16 mm.), n_D^{20} 1.4424, d_4^{20} 1.0521, M_D 76.07 (75.87), $[\alpha]_D^{20}$ −19.77°, $[M]_D^{20}$ −59.74°. $[\alpha]_D^{20}$ −22.45° (in ethyl alcohol, 6.000%), $[M]_D^{20}$ −67.86° (in ethyl alcohol). $[\alpha]_D^{20}$ −28.47° (in benzene, 5.126%), $[M]_D^{20}$ −86.03° (in benzene). $[\alpha]_D^{20}$ −18.17° (in cyclohexane, 5.952%), $[M]_D^{20}$ −54.91° (in cyclohexane).

Ethyl methylnonylmethylene-*d*-tartrate.

$C_{19}H_{34}O_6$ (358.27). (I) $R_1 = CH_3$, $R_2 = C_9H_{19}$, $R = C_2H_5$

To a mixture of 10 g. ethyl *d*-tartrate and 8.5 g. methyl nonyl ketone (Th. Schuchardt) was added 10 g. P_2O_5 in portions at 90° during one hour, and the reaction mixture was further heated at 80° for one hour. Yield 6 g. Colourless liquid boiling at 218° (15 mm.), n_D^{20} 1.4465, d_4^{20} 1.0086, M_D 94.82 (94.34), $[\alpha]_D^{20}$ −21.33°, $[M]_D^{20}$ −76.41°. $[\alpha]_D^{20}$ −21.38° (in ethyl alcohol, 7.5645%), $[M]_D^{20}$ −76.59° (in ethyl alcohol). $[\alpha]_D^{20}$ −26.03° (in benzene, 5.9822%), $[M]_D^{20}$ −93.44° (in benzene). $[\alpha]_D^{20}$ −18.93° (in cyclohexane, 5.4008%), $[M]_D^{20}$ −67.82° (in cyclohexane).

Methyl methylethylmethylene-*d*-tartrate.

$C_{10}H_{16}O_6$ (232.16). (I) $R_1 = CH_3$, $R_2 = C_2H_5$, $R = CH_3$

Methyl *d*-tartrate (15 g.), b.p. 163° (20 mm.), and 15 g. methyl ethyl ketone gave 9 g. pure colourless liquid boiling at 141° (15 mm.). n_D^{20} 1.4420, d_4^{20} 1.1607, M_D 52.92 (52.87), $[\alpha]_D^{20}$ −35.79°, $[M]_D^{20}$ −83.08°.

Propyl methylethylmethylene-*d*-tartrate.

$C_{14}H_{24}O_6$ (288.19). (I) $R_1 = CH_3$, $R_2 = C_2H_5$, $R = C_3H_7$

Propyl *d*-tartrate (15 g.), b.p. 171° (15 mm.), and 15 g. methyl ethyl ketone gave 9 g. pure product. To remove the unreacted propyl *d*-tartrate,

the ethereal extract of the mixture must be repeatedly washed with borax solution, since the ester is not so easily soluble in this solution as ethyl *d*-tartrate. Pale yellow liquid. Boiling point 167° (15 mm.). n_D^{20} 1.4399, d_4^{20} 1.0603, M_D 71.62 (71.25), $[\alpha]_D^{20}$ −30.07°, $[M]_D^{20}$ −86.65°.

Isopropyl methylethylmethylene-*d*-tartrate.

$C_{14}H_{24}O_6$ (288.19). (I) $R_1 = CH_3$, $R_2 = C_2H_5$, $R = (CH_3)_2CH$

To a mixture of 15 g. isopropyl *d*-tartrate, b.p. 155° (17 mm.), and 15 g. methyl ethyl ketone was added 15 g. phosphorus pentoxide at 70° in portions during one hour. The phosphorus oxide coloured deep brown but the liquid not so strongly. The liquid was decanted from the dehydrating reagent, and the unchanged ketone was evaporated off. The ethereal extract of the residual liquid was washed with N/2 KBO_2,[5] in order to remove the unreacted isopropyl tartrate, dried over sodium sulphate, and fractionated in vacuo. This process of purification was repeated once. Yield 8 g. Colourless liquid. Boiling point 115–117° (0.5 mm.). n_D^{20} 1.43321, d_4^{20} 1.0460, M_D 71.63 (71.25), $[\alpha]_D^{20}$ −30.32°, $[M]_D^{20}$ −87.36°.

Musashi Higher School, Itabashiku, Tokyo.

The Isomerization of Dimethyl Maleate by Hydrogen Bromide and by Hydrogen Chloride.

By Osamu SIMAMURA.

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Introduction. In the previous papers[1][2] it was reported that hydrogen bromide, in presence of oxygen, caused the isomerization of isostilbene to stilbene in the dark at room temperature either in absence of solvents or in benzene solution, while neither hydrogen bromide nor oxygen was active when present alone. Reduced nickel, which is in itself inactive to the isomerization of isostilbene to stilbene, was found also to co-operate with hydrogen bromide to accelerate the isomerization in absence of solvents, and another ferromagnetic metal, reduced iron, was shown to be capable of promoting the isomerization with hydrogen bromide, although the effect was smaller than that of reduced nickel.

It may be added here that subsequent experiments have shown that no isomerization of isostilbene to stilbene takes place with hydrogen

(5) The high efficiency of the use of KBO_2 in the separation has been clearly shown by quantitative studies, Y. Tsuzuki, this Bulletin, **13** (1938), 337.

(1) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507.
(2) Y. Urushibara and O. Simamura, *ibid.*, **13** (1938), 566.

chloride either alone or in presence of any of oxygen, reduced nickel, and benzoyl peroxide under essentially the same experimental conditions as described in the cited reports.[1][2]

The investigation has now been extended to the catalyzed isomerization of dimethyl maleate to dimethyl fumarate with the view of ascertaining whether oxygen co-operates with hydrogen bromide in accelerating the rearrangement just as that of isostilbene to stilbene, and it is the more interesting in view of the well-known conversion of maleic into fumaric acid by aqueous hydrogen halides,[3] which was investigated without taking account of the then unrevealed influence of oxygen. N. W. Hanson and D. M. Williams[4] showed that dimethyl fumarate was a by-product in the bromination catalyzed by hydrogen bromide of dimethyl maleate in carbon tetrachloride in the dark. It is, however, not clear whether dimethyl fumarate was produced by the sole action of hydrogen bromide or oxygen had any influence on it. In the present investigation it has been established that dimethyl maleate is isomerized to the fumarate by the catalytic action of hydrogen bromide and of hydrogen chloride and the presence of oxygen is indifferent to this catalyzed transformation under the present experimental conditions. The effect of reduced nickel, which is much weaker than that of oxygen in the case of isostilbene, has not been examined.

Materials. *Dimethyl Maleate.* 90 Grammes of maleic acid was dissolved in 1200 c.c. of methanol containing 75 g. of concentrated sulphuric acid and the solution was boiled on a water bath for ten hours. Then 450 c.c. of methanol was distilled off, the cooled reaction mixture poured into ice water and extracted repeatedly with carbon tetrachloride. The carbon tetrachloride layer was shaken with aqueous sodium carbonate solution, washed with water, and then dried with anhydrous sodium sulphate. After carbon tetrachloride was distilled off under the ordinary pressure the remaining oil was fractionated through a Widmer column and the middle fraction boiling at 88–88.5° under 6 mm. was collected (n_D^{20} 1.4429).

Hydrogen Bromide. Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a wash bottle containing tetralin and then through U-tubes filled with anhydrous calcium bromide and with anthracene respectively. For further purification, after bubbled through a bubble counter in which a part of the gas was liquefied by cooling with solid carbon dioxide and ether, the hydrogen bromide was collected in a receiver surrounded by liquid air. Then traces of incondensable gases were eliminated by repeated melting and solidification of the hydrogen bromide and evacuation of the vessel. Finally the gas was fractionated, a middle portion being collected in a gas burette. In some experiments hydrogen bromide was purified by passing through cold tetralin and over moist red phosphorus, anhydrous calcium bromide, and phosphorus pentoxide. It made no difference in the experimental results which of the methods was used in preparing hydrogen bromide.

(3) Skraup, *Monatsh.*, **12** (1891), 118.
(4) *J. Chem. Soc.*, **1930**, 1059.

Hydrogen Chloride. Hydrogen chloride was prepared from concentrated hydrochloric and sulphuric acids, dried by passing through concentrated sulphuric acid, condensed in a receiver cooled with liquid air, and then fractionated as in the case of hydrogen bromide.

Carbon Tetrachloride. A purest commercial product was boiled with alkaline potassium permanganate solution for six hours, washed with water, dried with calcium chloride, and then distilled over phosphorus pentoxide.

Experimental Procedures and Results. All the experiments were conducted in the dark at room temperature and the extent of reaction was examined under a photographic lamp.

(1) *Isomerization by Hydrogen Bromide.* In a glass tube with a capacity of 7–8 c.c. 0.2 c.c. of dimethyl maleate was taken, the air in the tube was evacuated, hydrogen introduced and again thoroughly evacuated; after the admission of 5 c.c. of hydrogen bromide (the volume of gas refers to the ordinary pressure) the tube was sealed off. In the course of one minute or two dimethyl maleate changed with an evolution of heat into a solid crystalline mass, which was then taken out of the tube by breaking it and crystallized from methanol, melting point 102–103°. In admixture with an authentic specimen of dimethyl fumarate the melting point showed no depression. In some experiments dimethyl maleate contained in a side tube attached to the reaction tube was vacuum-distilled into the latter under the complete exclusion of air, and the side tube having been severed by sealing off, the above-mentioned procedure was pursued; the results were the same. Catechol (5 mg.) added beforehand to dimethyl maleate had no influence on the isomerization by hydrogen bromide, whereas it is quite active in preventing that of isostilbene to stilbene caused by the joint action of hydrogen bromide and oxygen.

(2) *Isomerization by Hydrogen Bromide in Carbon Tetrachloride.* One c.c. of dimethyl maleate and 10 c.c. of carbon tetrachloride (with or without addition of catechol) were pipetted into a glass tube of 65 c.c. capacity, which was evacuated with simultaneous cooling with solid carbon dioxide and ether; the solidified mixture was then melted under evacuation and about 10 per cent of carbon tetrachloride was distilled off, thus traces of air being eliminated from the solution. Then 5–10 c.c. of hydrogen bromide was introduced, the tube sealed off and left to stand in the dark for a certain period. By a capillary seal attached to it the tube was connected to the vacuum line with a piece of rubber tubing, inside which the seal was broken by crushing from without. Introduction of hydrogen and subsequent evacuation enabled the complete removal of hydrogen bromide avoiding the complicating access of air. The carbon tetrachloride solution was washed with aqueous sodium carbonate solution and then with water, and dried over anhydrous sodium sulphate. On distilling off carbon tetrachloride and cooling the remaining mixture, of which Beilstein's test indicated the presence of bromine, dimethyl fumarate crystallized out. Though the experiments were of the qualitative nature the extent of isomerization was approximately estimated by noting the temperature at which the last crystals disappeared when the sample was heated very gradually in a water bath, and determining the composi-

tion from the composition-fusing point curve drawn by R. Schmidt.[5] Some of the results are tabulated in Table 1.

Table 1.

Exp. No.	Hydrogen bromide admitted (c.c.)	Catechol added (mg.)	Reaction time (hours)	Fumarate produced (per cent)
27	10	0	20.5	18
28	10	20	20.5	20
29	5	0	2.5	11
30	5	40	2.5	14

Table 2.

Exp. No.	Hydrogen bromide admitted (c.c.)	Oxygen added (c.c.)	Reaction time (hours)	Fumarate produced (per cent)
47	5	0	5	15
48	5	5	5	13
49	5	0	24.5	20
50	5	5	24.5	19

As the reaction in carbon tetrachloride was much slower than in absence of solvents the effect of oxygen on the reaction could be conveniently examined. In the experiments with added oxygen the reaction mixture, after removal of hydrogen bromide, was immediately evaporated and the composition estimated (Table 2). The increase of the amount of oxygen added up to 50 c.c. had no perceptible influence on the results. In every pair of conjugate runs a difference of one or two per cent in the amount of fumarate produced was observed; in all likelihood this might not be a real difference in view of the experimental accuracy and the conclusion is that oxygen and catechol have no influence on the isomerization caused by hydrogen bromide of dimethyl maleate to the fumarate.

(3) *Isomerization by Hydrogen Chloride.* The experimental details were quite the same as described in (1). It was about one hour before the precipitation of dimethyl fumarate set in and the reaction was slowly brought to completion in the course of more than ten hours. The addition of catechol caused no alteration of the progress of the reaction. In presence of a larger amount of hydrogen chloride the isomerization was of course rapid: in a vessel with a capacity of 65 c.c. 0.2 c.c. of dimethyl maleate and 50 c.c. of hydrogen chloride were sealed; the isomeric ester began to deposit in five minutes, and the conversion was nearly completed in 40–45 minutes.

(4) *Isomerization by Hydrogen Chloride in Carbon Tetrachloride.* The procedure described in (2) was closely followed substituting hydrogen chloride for the bromide. The results are summarized in Table 3.

(5) *Z. physik. Chem.*, B, **1** (1928), 209.

Table 3.

Exp. No.	Hydrogen chloride admitted (c.c.)	Oxygen added (c.c.)	Reaction time (hours)	Fumarate produced (per cent)
7	5	0	21	4
8	25	0	42	18
9	25	20	42	17

Discussion. Numerous investigations on the isomerization of the maleinoid to the fumaroid compounds are available and the action of halogens which are effective in the light in causing the transformation is attributed to halogen atoms formed by the absorption of light quantum. The inversion is supposed to occur in a molecule formed by the addition of the halogen atom thus produced to the ethenoid linkage, the subsequent elimination of the halogen atom regenerating the isomeric ethenoid form.

M. S. Kharasch, J. V. Mansfield, and F. R. Mayo[6] have observed, that isostilbene is isomerized to stilbene by hydrogen bromide either in the light or in the presence of a peroxidic substance and not by hydrogen bromide alone, that the catalyzed transformation is prevented by anti-oxidants (e.g. hydroquinone, catechol), and that hydrogen chloride is ineffective in causing the isomerization under any of the conditions. Thus they have been led to the belief, that in this reaction the active catalysts are bromine atoms which are produced by the action of a peroxide or light on hydrogen bromide. Further, Y. Urushibara and O. Simamura[1][2] have reported that oxygen, too, is effective in activating hydrogen bromide to isomerize isostilbene to stilbene.

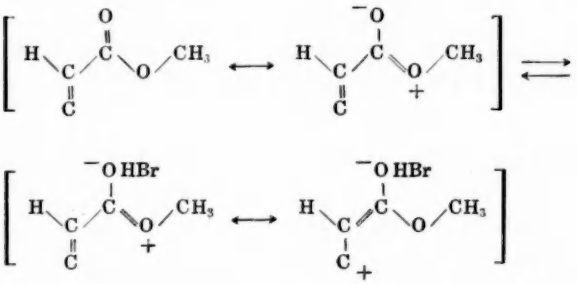
As detailed in the experimental part of the present communication dimethyl maleate is converted into the fumarate by hydrogen bromide and by hydrogen chloride and the influence of oxygen is not perceptible. However, the possibility of the influence of oxygen cannot totally be excluded. The effect of oxygen, if any, must be negligibly small compared with that of hydrogen bromide alone; but the possibility of the effectiveness of oxygen in the case of hydrogen chloride can readily be ruled out on the basis of the stability of the latter toward oxygen and by the experimental fact that hydrogen chloride and oxygen do not cause the isomerisation of isostilbene. Thus the conversion of dimethyl maleate into the fumarate by hydrogen halides belongs to another type of catalyzed cis-trans isomerization apparently distinct from that of isostilbene by hydrogen bromide and oxygen.

Concerning the mechanism of the conversion of maleic into fumaric acid caused by aqueous hydrogen halides several speculations are available. From a kinetic study of the reaction E. M. Terry and L. Eichelberger[7] have proposed a hypothesis, that the catalyst goes into interaction with carboxyl groups and "saturates" them, and that this removes the stabilizing influence of the carboxyl group upon the double bond, facilitating the

(6) *J. Am. Chem. Soc.*, **59** (1937), 1155.
(7) *J. Am. Chem. Soc.*, **47** (1925), 1402.

activation of the latter to the isomeric change. This idea of the interaction of the group adjacent to double bond with the catalyst may be applicable to account for the mechanism of the isomerization of dimethyl maleate under consideration, because hydrogen halides do not isomerize isostilbene but dimethyl maleate, and it seems highly probable that the carbomethoxyl group plays an important role. Moreover, as the experiments have been made either without solvents or in non-hydroxylic one, the hypothesis can be stated in a more concrete form: the association of the ester group with hydrogen halides by means of, for example, hydrogen bond formation deforms more or less the electronic configuration of the molecule, and thus destroys the rigidity of the double bond. In support of the idea that the addition of the acids to ester group takes place, a work of O. Maass and D. McIntosh[8] may be cited, who confirmed the existence of an addition compound $CH_3CO_2C_2H_5 \cdot HBr$, and further W. Gordy and P. C. Martin[9] concluded the formation of hydrogen bond between hydrogen chloride and ethyl acetate from a study of the infrared absorption spectra.

It seems to be hardly possible, that the addition should take place at the oxidic oxygen as W. A. Waters[10] seems to believe, because then this oxygen atom would have to gain in positive charge against the opposing influence of the carbonyl group. On the other hand, if in the carboxylic ester molecule the resonance effect is considerable as contended by S. Mizushima and M. Kubo,[11] more negative charge will concentrate on the carbonyl oxygen atom than otherwise; thus the association with hydrogen halides may take place through the carbonyl oxygen, and the subsequent activation of the double bond as formulated below:



The formation of co-ordination link through hydrogen atom and carbonyl group prior to the isomerization has already been postulated by G. R. Clemo and S. B. Graham[12] who have noticed the catalytic action of primary and secondary amines, especially of piperidine, on the isomerization of dimethyl maleate. Their assumption seems to be appropriate in view of the analogy between the catalytic actions of piperidine

(8) *J. Am. Chem. Soc.*, **34** (1912), 1272.
(9) *Phys. Rev.*, **52** (1937), 1075.
(10) W. A. Waters, "Physical Aspects of Organic Chemistry," 2nd Ed., 266, London (1937).
(11) This Bulletin, **13** (1938), 174.
(12) *J. Chem. Soc.*, **1930**, 213.

and hydrogen halides, the former, too, being ineffective in causing the transformation of isostilbene to stilbene as confirmed by the present author.

Summary.

(1) No isomerization of isostilbene to stilbene occurs with hydrogen chloride in the presence of either reduced nickel or oxygen.

(2) Hydrogen bromide and hydrogen chloride cause the isomerization of dimethyl maleate to the fumarate either in absence of solvents or in carbon tetrachloride solution.

(3) Oxygen has no effect on the isomerization of dimethyl maleate by hydrogen halides.

(4) The isomerization of dimethyl maleate by hydrogen halides belongs to another type of catalyzed cis-trans isomerization apparently distinct from that of isostilbene by hydrogen bromide and oxygen.

(5) A hypothesis has been proposed concerning the mechanism of the isomerization of dimethyl maleate caused by hydrogen halides.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragements throughout the work and to Prof. S. Mizushima for valuable advices. Thanks are also due to the Japan Society for the Promotion of Scientific Research (Nippon Gakujutsu Shinko-Kwai) and to Ozi Seisi Company for grants.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.